those which are associated with two surfaces are obtained up to the second order inclusive. The necessary calculations are laborious. In the case of the invariants, which are actually of the third order, only the results are stated; they were obtained by solving fifty-seven simultaneous partial differential equations.

It is known from Lamé's investigations that there are six equations characteristic of the fundamental magnitudes when the independent variables are the parameters of a triply-orthogonal system of surfaces. Cayley proved that there are similarly six equations when the independent variables are the parameters of three families of surfaces not orthogonal to one another. These six equations, as formed by Cayley, arise in the course of the construction of the invariants of the third order.

In the later part of the memoir, the invariants up to the second order inclusive are geometrically interpreted. Those of the third order have not yet been similarly interpreted; geometrical considerations are adduced to show that, when the significance of these invariants is established, two new fundamental equations among the quantities connected with a surface will be found to exist.

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"The Ultra-violet Spectrum of Radium." By Sir WILLIAM
CROOKES, F.R.S.   Received August 1, 1903.

[PLATES 16—18.]

The spectrum of radium has been examined and the wave-lengths of many of its lines given by several observers, amongst whom I may include Exner and Haschek,* Berndt,† Demarçay,‡ and Runge.§

Between these observers, however, there are great discrepancies, lines given by one being absent in other lists, and the wave-lengths even of strong lines varying between wide limits.   Being in possession of perhaps the purest radium hitherto employed for spectrum work, I have used some of it in photographing its ultra-violet spectrum. The negatives so obtained have enabled me to get measurements from which the wave-lengths of the lines have been calculated with an accuracy only limited by the accuracy of the iron lines used as standards.

* Franz Exner and E. Haschek, 'Wien Akad. Sitzber.,' vol. 110, July, 1901; 'Chem. News,' vol. 86, p. 247.

† G. Berndt, 'Physikalische Zeitschrift,' 2 Jahrg., No. 12;  'Chem. News,' vol. 83, p. 77.

‡ Demarçay, 'Comptes Rendus,' vol. 129, p. 716; vol. 131, p. 258.

§ C. Runge, 'Astrophysical Journal,' vol. 12, p. 1.

The spectrograph itself is a five-prism quartz instrument which I have had in use since 1894. A general idea can be gained of the arrangement of the spectrograph from the accompanying outline plan (fig. 1). The light from the source, $a$, passes first through the condenser, $b$, on to a slit, $c$, thence to the collimating lens, $d$, and

FIG. 1.
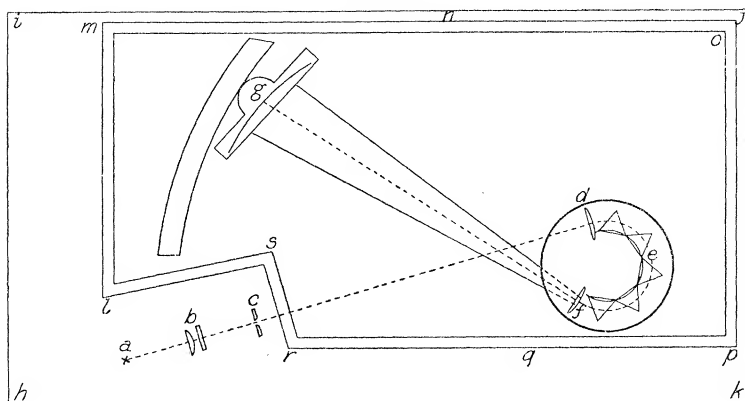


round the train of prisms, $e$. It then passes through the camera lens, $f$, whence it falls on the sensitive film in the holder, $g$. The whole apparatus is mounted on a planed cast-iron table, $h$, $i$, $j$, $k$, $49\frac{1}{2}$ inches long, 31 inches wide, and $1\frac{1}{4}$ inches thick. The prisms, lenses, and photographic film-holder are enclosed in a large wooden framework, $l$, $m$, $n$, $o$, $p$, $q$, $r$, $s$, having aluminium shutters on each side, so that the inner adjustments can be effected easily. The height of the enclosure is 28 inches, and the whole is perfectly light-tight when the shutters are down. Outside the dark enclosure, in the space $h$, $l$, $s$, $r$, are situated the arrangements for producing the light to be examined, the optical condensers, and the slit.

An electrical condenser of 180 square inches is intercalated in the secondary circuit, and a coil of twelve turns of well-insulated wire, each turn being 12 inches in diameter, is interposed in the path of the secondary current. This introduction of self-induction in the circuit suppresses most of the air lines, and gives the metal lines on a black background.

The optical efficiency of a spectrograph depends in no small degree on the way in which the source of light is presented to the slit. If the electrodes are too far apart there is distortion, owing to each pole forming its own luminous centre, and if the spark is close to the slit we have to contend with other irregularities; the image is not clear, and the lines are often confused and blurred. If the spark is

moved away from the slit the spectrum gains in definition ; the greater the distance between the light and the slit the finer is the sharpness and definition of the lines, but at the same time the loss of light is great.   This loss of light, however, may be obviated in great measure, with considerable improvement of the definition, by inserting optical condensers between the spark and the slit.   I use two condensers of quartz, plano-cylindrical, one being double the focus of the other, the axes intersecting each other at an angle of 90° ; the object being to concentrate a line instead of a point of light on the slit.   All optical condensers waste much light.   I use them more to obtain well-defined images than to abridge the time of exposure.

The slit is made of two shallow-angled quartz prisms, as I have already described,* and the distance apart of the jaws is generally 0·01 mm.

The quartz prisms, of which there are five, are of 60°, made in two halves of 30° each, according to Cornu's plan, one half being right-handed and the other half left-handed.   The contact surface of both bisects the refractive angle of the entire prism, and is placed perpendicularly to the crystalline axis of both prisms.   In this way duplication of lines is avoided.

The sensitive film-holder must be set at an angle varying with the portion of the spectrum being photographed, as the focus of the less refrangible is longer than that of the more refrangible rays.   Moreover, the focal plane is not flat, so the film itself must follow the diacaustic curve, or the lines on it will not all be in focus together.†   For this reason glass plates cannot be used, and celluloid films are employed.

To obtain the best definition of any desired line for measurement, expose for a long time and develop briefly, using plenty of potassium bromide in the pyro developer.   It is impossible to photograph properly the whole spectrum with a single exposure, so as to have it well defined in all parts, since the brightest lines are over exposed and blurred sideways before the faint ones are impressed.   This important fact is too generally lost sight of in spectrum photography.

For correct determination of wave-lengths, it is necessary to photograph on the same film the spectrum of a metal whose lines are known. I generally use iron for this purpose ; it has the advantage of giving a large number of very fine lines, the wave-lengths of which have been accurately measured, and not being very volatile, the poles do not rapidly wear away.   By means of diaphragms close to the slit the experimental and the standard spectra are photographed on the same

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* 'Chemical News,' vol. 71, p. 175, April 11, 1895; 'Roy. Soc. Proc.,' vol. 65, p. 241.

† 'Chem. News,' vol. 72, p. 87, August, 1895; and vol. 74, p. 259, November, 1896 ; 'Proc. Roy. Soc.,' vol. 65, p. 242.

film, overlapping for about 1 mm. in the centre.*    The photographs
are then transferred to a measuring machine, and from the figures
thus obtained the wave-lengths are calculated.

The radium was used in the form of nitrate, a well-crystallised salt
easily soluble in water.    The induction spark was taken between
platinum poles partly immersed in a strong solution of the salt.    On
this account the nitrate was used in preference to the chloride.    Much
platinum is always dissolved when the poles are sparked in a solution
of a chloride, while with nitrates this does not occur to the same
extent.

The solution was strong, and slightly acid with nitric acid.    Many
forms of spark tube were tried before a satisfactory form (shown in
fig. 2) was devised.    AB is a tube of hard Jena glass, with a bulb at

FIG. 2.
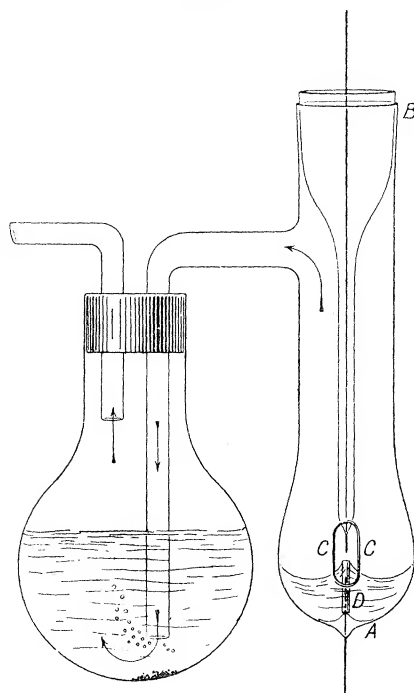


the lower end.    At the bottom of the bulb a platinum wire is sealed
in, and in the upper part of the tube, at B, a short piece of tube is
ground in to form a stopper.    A long platinum wire passes through
from this stopper, bare at the upper part, and guarded with glass

inside the bulb tube.   A hole, CC, is made at one side of the bulb to form a window, and a piece of platinum tube is put round the lower platinum wire at D, so that its upper end is about 3 mm. above the end of the wire it surrounds, and a millimetre below the centre of the window, CC.   The upper wire should be about 1 mm. from the top of the platinum tube surrounding the lower wire.   Any solution put in the lower part of the bulb is sucked up by capillarity to the top of the platinum tube, and an induction spark between the two wires gives a spectrum of any metal in solution.   When exposures of more than ten minutes or so are required, it is necessary to introduce fresh solution to keep the level in the bulb constant.   This is easily done during the exposure by means of a small pipette.   The splash of the spark throws drops of liquid for some distance, and the heat and decomposition cause nitric acid to come off.   These are objectionable when falling on delicate apparatus, and they cause great waste of solution, which with rare bodies is to be avoided; to prevent this a branch tube is sealed in near the top of the spark tube, dipping to the bottom of a flask through a cork.   Another tube passes just through the cork and is connected with an aspirator.   During the sparking operation a rapid current of air is drawn in through the window, and all splashes and vapours are washed through the water in the wash-bottle. Thus the acid fumes are kept from injuring the apparatus, and the valuable salt is saved in the wash water.

The presence of platinum lines is due to the platinum poles between which the spark is taken.   They are easily identified by photographing a platinum spectrum and a platinum-radium spectrum on the same plate, slightly overlapping one another.   The platinum being common to both, gives continuous lines across the two spectra, while the radium lines only appear in one spectrum.   Radium being purified from barium by a tedious process of fractional crystallisation of the bromides is almost certain to show barium lines in its spectrum.   I have only been able to use about a grain of perfectly pure radium bromide, all other samples containing traces of barium.

Owing to the length of the spectrum and the necessity of having the lines near the position of minimum deviation to get the greatest sharpness, each photograph is limited to a small extent of spectrum, and eight exposures are needed to take in the whole ultra-violet spectrum, and as far into the visible part as the plates are sensitive to.

The following table gives the wave-lengths of all the lines ascribed to radium by different observers.   Many of the early observations are necessarily imperfect, owing to the enormous difficulty of preparing radium compounds of sufficient strength to show a photographed spectrum.   And when sufficient concentration was obtainable, the observations were necessarily limited, owing to the minute amount available rendering verification difficult.

Wave-lengths of the Radium Lines according to the different
Authorities.

| Runge. | De-marçay. | Exner and Haschek. | W. Crookes. | Inten-sity. | Remarks. |
|---|---|---|---|---|---|
| | | 2512 ·46 | | | I cannot see this line on my photo-graphs. |
| | | | 2709 ·06 | 20 | This is close to an iron line, 2709·14. |
| | | 2736 ·2 | | | I cannot see this line on my photo-graphs. |
| | | 2813 ·60 | 2813 ·876 | 30 | Comes between a fine pair of platinum lines. |
| | | 2816 ·25 | | | Probably a platinum line, 2816·1. |
| | | 2831 ·98 | | | I cannot see this line on my photo-graphs. |
| | | 2877 ·10 | | | Probably an iridium line, 2877·1. |
| | | 2908 ·0 | | | Probably a platinum line, 2908·1. |
| | | 2976 ·17 | | | Probably a platinum line, 2975·9. |
| | | 3079 ·97 | | | Probably a platinum line, 3079·8. |
| | | 3126 ·53 | | | I cannot see this line on my photo-graphs. |
| | | 3541 ·77 | | | Ditto. |
| 3649 ·77 | 3649 ·6 | 3649 ·33 | 3649 ·712 | 70 | A very strong radium line. |
| | | | 3809 ·393 | 10 | A faint radium line. |
| | | | 3812 ·170 | 5 | A faint radium line. |
| 3814 ·591 | 3814 ·7 | 3814 ·62 | 3814 ·661 | 100 | The strongest line in the radium spectrum. |
| | | 3861 ·77 | | | I cannot see this line on my photo-graphs. Exner and Haschek include it in their radium lines, but in a note say it is not a line of radium. |
| | | | 3961 ·627 | 5 | A faint radium line. |
| | | 3993 ·25 | | | Probably a barium line, 3993·69. |
| | | | 4010 ·397 | 10 | A faint radium line. |
| | | 4053 ·81 | 4053 ·124 | 10 | A faint radium line. |
| 4341 ·0 | 4340 ·6 | | 4340 ·619 | 5 | A faint radium line. |
| | 4364· 2 | | | | I cannot see this line on my photo-graphs. |
| 4436 ·45 | 4436 ·1 | | | | Probably a platinum line, 4437·5. |
| | 4458 ·0 | | | | Demarçay says this is the centre of a nebulous band, which be-gins at 4463·7, has a maximum from 4453·4 to 4455 2, and ends at 4390·0. I cannot see this on my photographs. |
| 4533 ·33 | 4533 ·5 | | | | I cannot see this line on my photo-graphs. |
| | 4600 ·3 | | | | Demarçay says (with a query) that this line does not belong to radium. I cannot see it on my photographs. |
| | 4627 ·4 | | | | Demarçay says this is the centre of a nebulous line, which be-gins sharply at 4621·9, has a maximum at 4627·5, and ends about 4631. I cannot see it on my photographs. |
| | 4641 ·9 | | | | I cannot see this line on my photo-graphs. |

## Wave-lengths of the Radium Lines—*continued.*

| Runge. | De-marçay. | Exner and Haschek. | W. Crookes. | Inten-sity. | Remarks. |
|---|---|---|---|---|---|
| 4682·346 | 4683·0 | 4682·41 | 4682·149 | 25 | A strong radium line. |
|  | 4692·1 |  |  |  | I cannot see this line on my photographs. |
|  | 4699·8 |  |  |  | Ditto. |
|  | 4726·9 |  |  |  | Ditto. |
|  |  | 4781·4 |  |  | Ditto. |
| 4826·14 | 4826·3 |  | 4825·896 | 15 | A strong radium line. |
| 5813·9 |  |  | 5813·9 |  | This is a strong citron line, outside the range of my photographs. |

Measurements are taken of the exact distances apart of the radium lines and certain adjacent iron lines used as standards. By using a formula, first communicated to the British Association by Sir George Stokes, the wave-lengths of the unknown lines can be calculated. At the time the formula was given it was sufficiently accurate for the instrumental means employed for photographing spectra, but the formula only gave approximate results, and the accuracy of determination of wave-lengths has since improved so much that a correction is required to the original formula. Sir George Stokes, before whom I placed the difficulty in June, 1895, quickly solved it in a satisfactory manner. The usual formula requires the positions of two standard lines of known wave-length, $n_1$ and $n_3$, on each side of the unknown line, $n_2$. To make the small correction, Sir George advised me to take a third line of known wave-length, chosen well removed from the selected known lines $n_1$ and $n_3$. If chosen in the interval 1—3 it had better not be greatly distant from the middle. There is, however, very wide latitude of choice in this respect. All these lines must be photographed and measured in the usual way. Calculate the approximate wave-length of the unknown line by the original formula, and then calculate the approximate wave-length of the third known line by the same formula, *as if it were unknown*, using the two original standards for this purpose also. We have now the approximate wave-length of a known line, as given by the formula, and also its true wave-length The difference between these two values leads (*infra*, p. 303) to the correction to apply to the approximate value of the unknown line.

It often happens that four or more lines are well placed for use as standards. If any three of these be taken, and from them the positions of the other lines be calculated, it will sometimes be found that there is a small residual error in some of them. In such a case the error can be minimised by adjusting the value of the three primary standards so

that the sum of the errors on all the lines is a minimum, and in no individual case is very great.    Then, with these three corrected standards, the unknown lines may be calculated with confidence to seven figures.

With few exceptions my standards are the most recent published by Rowland.    He has given two sets of " Standard Wave-lengths," one in ' Astronomy and Astrophysics,' vol. 12, p. 321, published in 1893 ; the other in the ' Astrophysical Journal,' vol. 1, No. 1, January, 1895, to vol. 5, No. 3, March, 1897, and vol. 6, No. 5, December, 1897.    Any systematic or accidental error found to occur in Rowland's figures will require a corresponding correction of my own wave-lengths.    Assuming Rowland's wave-lengths to be correct, I can follow his seven-figure standards with a probable error of $\pm$ 0·002 at the most refrangible end, and one of $\pm$ 0·01 at the least refrangible end.    The average error being $\pm$ 0·005.    But on the assumption that all Rowland's measurements are incorrect by a variable amount, as rendered probable by the recent work of Fabry and Perot,[*] a correction will have to be made which will affect the sixth figure.[†]

For the reduction of the lines 4682·149 and 4825·896, there being no well-defined iron lines suitable for measurement, I have used some strong zinc and cadmium lines, which also have been measured by Rowland.

The following is the method of calculation I now employ :—

$$\begin{array}{cc} n_1 & \lambda_1 \\ n_2 & \lambda_2 \\ n_3 & \lambda_3 \\ n_4 & \lambda_4 \end{array}$$

$n_1$ and $n_3$ are scale positions on the measuring machine of standard lines of known wave-lengths, $\lambda_1$ and $\lambda_3$.

$n_2$ is the scale position of the line whose wave-length is required ($\lambda_2$).

$n_4$ is the scale position of an additional standard line whose wave-length is known.    It is used for obtaining the correction to apply to the approximate wave-length of $\lambda_2$.

$E_2$ and $E_4$ are the calculated errors obtained for $\lambda_2$ and $\lambda_4$, which have to be added to or subtracted from $\lambda_2$ or $\lambda_4$ to get them accurate.

For the tedious calculations involved in the reduction of the wave-lengths I am indebted to my son, Mr. Bernard H. Crookes, M.Sc.

* ' Comptes Rendus,' vol. 132, No. 21, May 28, 1901.

† Measuring a ruled glass micrometer in my measuring machine I find the average of ten scale readings can be relied on as not more than 0·00002 inch in absolute error on an average, with occasional errors of double this amount, and of course many errors of less, or zero.    The effect of an error of this magnitude represents an error of 0·0025 in the wave-length at one end of the spectrum, and one of 0·011 at the other end.

*Rule.*

First calculate the approximate value of $\lambda_2$ by the following formula :—

$$\frac{\lambda_3{}^2\lambda_1{}^2(n_3 - n_1)}{\lambda_1{}^2(n_2 - n_1) + \lambda_3{}^2(n_3 - n_2)} = \lambda_2{}^2 \text{ (approx.)} \quad \ldots\ldots\ldots \quad (1).$$

Next, in a similar way, find the approximate value of $\lambda_4$, using the following formulæ :—

$$\frac{\lambda_3{}^2\lambda_1{}^2(n_3 - n_1)}{\lambda_1{}^2(n_4 - n_1) + \lambda_3{}^2(n_3 - n_4)} = \lambda_4{}^2 \text{ (approx.)} \quad \ldots\ldots\ldots \quad (2).$$

Then

$$\lambda_4 \text{ (true)} = \lambda_4 \text{ (approx.)} \pm E_4.$$

Now calculate $E_2$ by the following equation :—

$$\frac{\text{(Approx.) } \lambda_2{}^3(n_2 - n_1)(n_3 - n_2)}{\text{(Approx.) } \lambda_4{}^3(n_4 - n_1)(n_3 - n_4)} E_4 = E_2 \quad \ldots\ldots\ldots \quad (3).$$
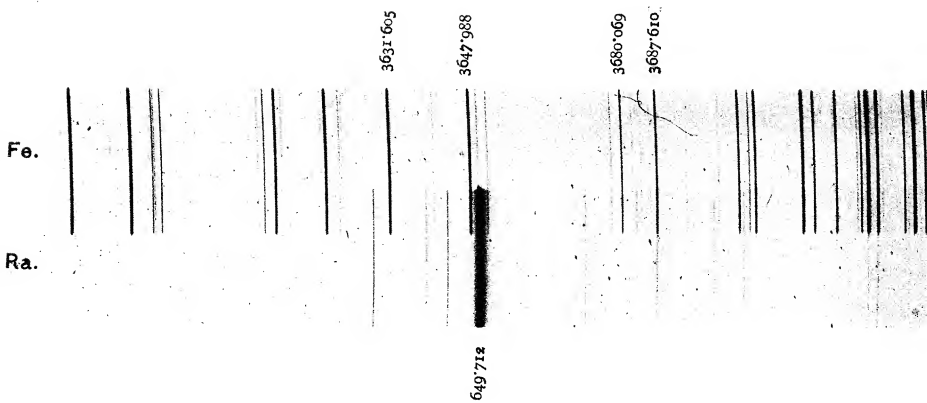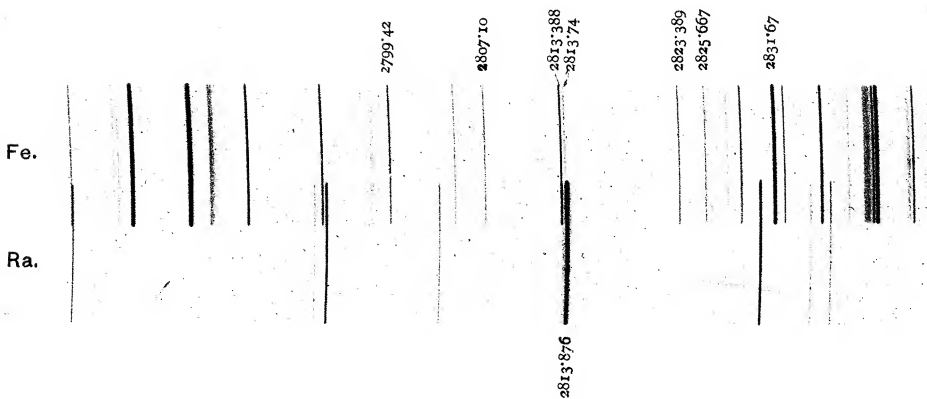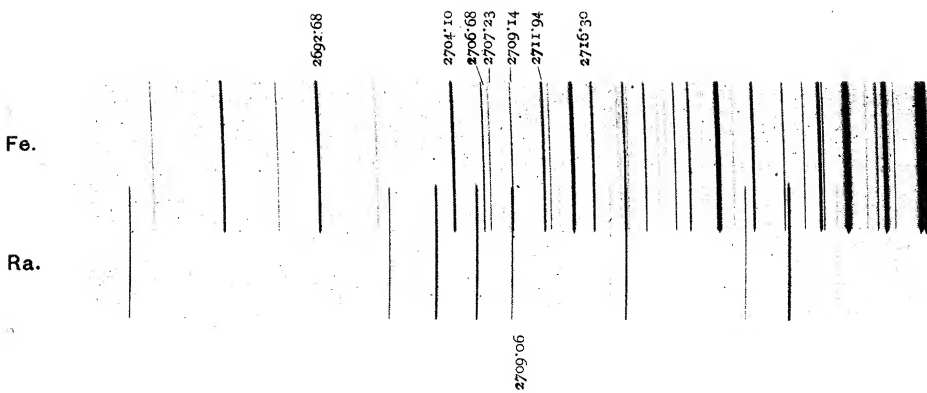
Then

$$\text{(Approx.) } \lambda_2 \pm E_2 = \lambda_2.$$

[In fact, writing $y$ for $\lambda^{-2}$, of which the refractive index is a function, and $x$ for $n$, the graph of the relation between $y$ and $x$ may in this neighbourhood be identified with a parabola. The formulæ (1) and (2) neglect the effect of its curvature, by taking the points 2 and 4 to be on the chord connecting the points 1 and 3. The corrections $E_2$ and $E_4$ are thus connected with the distances from the points on this chord to the true points on the curve by the formula $\delta y = -2E/\lambda^3$; and the formula (3) connecting them is the expression of a well-known geometrical property of a parabola.]
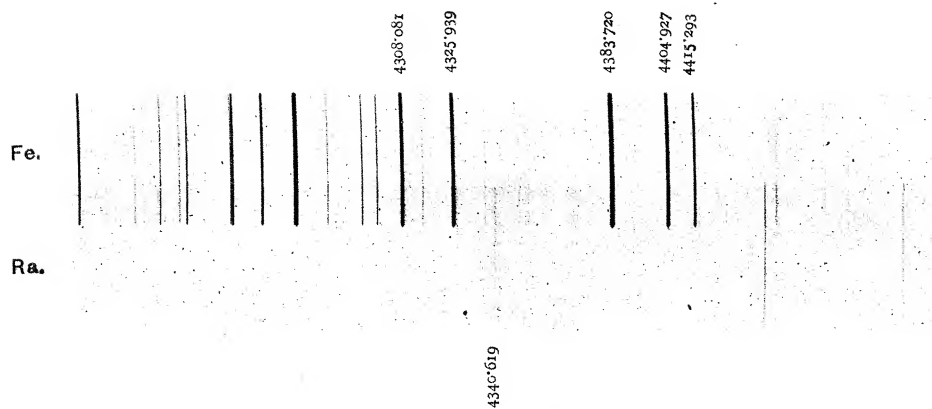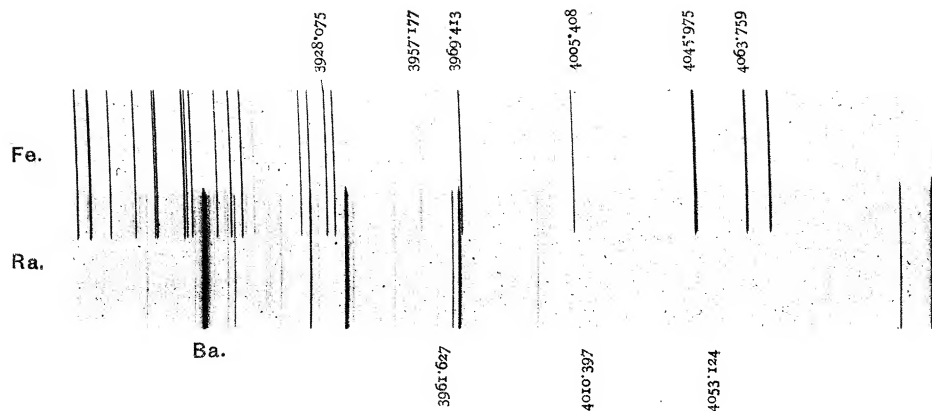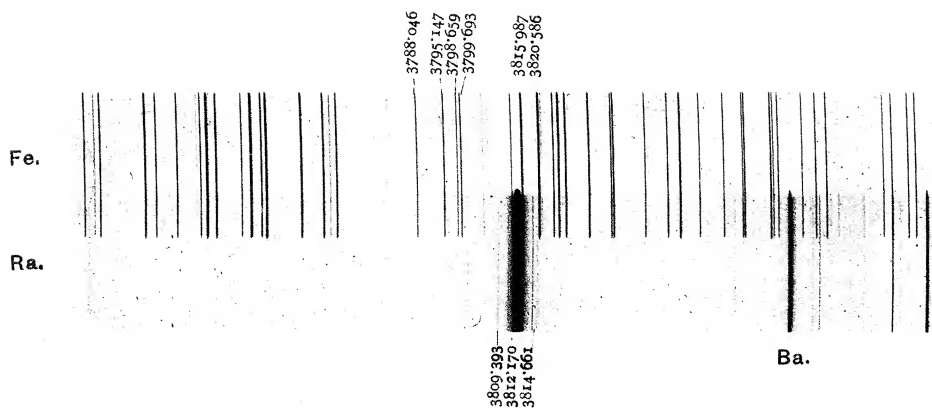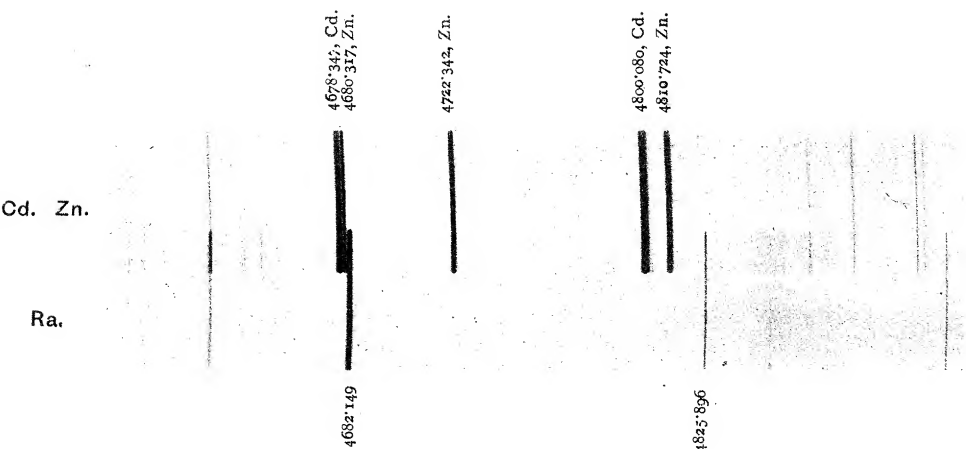
*Example.*

Calculate a radium line from adjacent iron lines as standards.

$$n_1 = 0\cdot000000. \qquad \lambda_1 = 2813\cdot388 \text{ (Rowland)}.$$
$$n_2 = 0\cdot005310. \qquad \lambda_2 = \text{A radium line}.$$
$$n_4 = 0\cdot107143. \qquad \lambda_4 = 2823\cdot389 \text{ (Rowland)}.$$
$$n_3 = 0\cdot131020. \qquad \lambda_3 = 2825\cdot667 \text{ (Rowland)}.$$

| | | | | |
|---|---|---|---|---|
| $2 \log \lambda_1$ | $6\cdot8984593$ | | $2 \log \lambda_3$ | $6\cdot9022420$ |
| $\log 0\cdot00531$ | $\bar{3}\cdot7250945$ | | $\log 0\cdot125710$ | $\bar{1}\cdot0993698$ |
| $\log 42029\cdot46$ | $4\cdot6235538$ | | $\log 1003718\cdot32$ | $6\cdot0016118$ |
| | | | $42029\cdot46$ | |
| | | | $\log 1045747\cdot78 =$ | $6\cdot0194269$ |

$$
\begin{array}{lr}
2 \log \lambda_3 & 6 \cdot 9022420 \\
2 \log \lambda_1 & 6 \cdot 8984593 \\
\log 0 \cdot 131020 & \bar{1} \cdot 1173376 \\
\hline
\log \text{ numerator} & 12 \cdot 9180389 \\
\log \text{ denominator} & 6 \cdot 0194269 \\
\hline
2) & 6 \cdot 8986120 \\
\hline
& 3 \cdot 4493060 = \log 2813 \cdot 883 = \lambda_2 \ (\text{approx.})
\end{array}
$$

$$
\begin{array}{lr}
2 \log \lambda_1 & 6 \cdot 8984593 \\
\log 0 \cdot 107143 & \bar{1} \cdot 0299638 \\
\hline
\log 848053 \cdot 20 & 5 \cdot 9284231 \\
\end{array}
\qquad
\begin{array}{lr}
2 \log \lambda_3 & 6 \cdot 9022420 \\
\log 0 \cdot 023877 & \bar{2} \cdot 3779798 \\
\hline
\log 190643 \cdot 44 & 5 \cdot 2802218 \\
848053 \cdot 20 & \\
\hline
\log 1038696 \cdot 64 = & 6 \cdot 0164887
\end{array}
$$

$$
\begin{array}{lr}
\log \text{ numerator} & 12 \cdot 9180389 \\
\log \text{ denominator} & 6 \cdot 0164887 \\
\hline
2) & 6 \cdot 9015502 \\
\hline
& 3 \cdot 4507751 \quad \log 2823 \cdot 418 = (\text{approx.}) \ \lambda_4 \\
\text{But---} & \lambda_4 = 2823 \cdot 389 \\
\therefore & E_4 = \quad 0 \cdot 029
\end{array}
$$

$$
\begin{array}{lr}
3 \log \lambda_2 & 10 \cdot 3479 \\
\log 0 \cdot 005310 & \bar{3} \cdot 7251 \\
\log 0 \cdot 12571 & \bar{1} \cdot 0994 \\
\hline
\log \text{ numerator} & 7 \cdot 1724 \\
\log \text{ denominator} & 9 \cdot 2979 \\
\hline
& \bar{3} \cdot 8745 \\
\end{array}
\qquad
\begin{array}{lr}
3 \log \lambda_4 & 10 \cdot 3523 \\
\log 107143 & \bar{1} \cdot 0300 \\
\log 0 \cdot 023877 & \bar{2} \cdot 3780 \\
\hline
& 7 \cdot 7603 \\
\log 0 \cdot 029 & \bar{2} \cdot 4624 \\
\hline
& 9 \cdot 2979
\end{array}
$$

$$
\therefore E_2 = \quad 0 \cdot 007
$$
$$
\lambda_2 = 2813 \cdot 876
$$

## THE ULTRA-VIOLET SPECTRUM OF RADIUM.

The Collotype illustrations are from the original negatives, and are entirely untouched. The grain of the process somewhat diminishes the sharpness of the lines.

To economise space and avoid unnecessary complications, I have given photographs of only that part of the spectrum adjacent to the radium lines. Had the whole spectrum been given as photographed, the length would have extended to more than 10 feet.

The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to Rowland's latest measurements. The lower halves contain the radium lines, with their wave-lengths as calculated from the iron standards. The other lines on the lower halves are chiefly platinum lines. On the 4th and 5th photograph a strong barium line is shown at wave-length 3891·97 (Rowland), or 3892·42 (Exner and Haschek).

In the part of the spectrum shown on the last strip there are no iron lines suitable for standards. Here, therefore, I have used some good lines of zinc and cadmium the wave-lengths of which are given in Rowland's latest table.

Fe.

Ra.

Ba.

Fe.

Ra.

Ba.

Fe.

Ra.

Cd. Zn.

Ra.